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Optical second harmonic generation study of vicinal Si(111) surfaces

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The appearance of well defined steps on vicinal Si(111) surfaces has a very pronounced effect on the rotational anisotropy of the Second Harmonic Generation from these surfaces. This effect can be explained by the lowering of the surface symmetry and an enhancement of the nonlinear susceptibility at these steps. By modifying the surface in this way, surface and bulk contributions to the SHG could be determined separately.

1. Introduction

Second-order nonlinear optical techniques like Second Harmonic Generation (SHG) have recently been developed as extremely versatile and sensitive surface and interface probes [1,2]. Optical surface probes have some definitive advantages: they are applicable to any interface accessible by light, including those between dense media, while their high temporal resolution allows in situ monitoring of surface dynamics [3–5]. For the development and application of SHG for interface studies, a better understanding of the nonlinear sources and the relation between the electronic structure of solids and surfaces and their respective nonlinear optical responses is required. Though SHG derives its surface sensitivity from the dipole allowed surface term to the SHG, that is forbidden in the bulk of centrosymmetric media, higher-order (quadrupole) bulk terms are allowed and appear as effective surface contributions. We have found a novel way to separate these bulk and surface contributions by modifying the surface by a well defined step structure. Results on oxidized Si(111) wafers show this to be a successful scheme.

2. Theory

SHG arises from the nonlinear polarization $P(2\omega)$ induced by an incident laserfield $E(\omega)$. The surface allowed dipole contribution can be written as:

$$P_{S,i}(2\omega) = \chi_{S,ijk}^{(2)} E_j(\omega) E_k(\omega), \quad (1)$$

where $\chi_S^{(2)}$ is a second-order nonlinear susceptibility tensor reflecting the structure and symmetry properties of the surface layer. The bulk nonlinear polarization of cubic media excited by a single incident field can be written as [6]:

$$P_{B,i}(2\omega) = \gamma \nabla_i (E(\omega) \cdot E(\omega)) + \xi E_i(\omega) \nabla_i E_i(\omega). \quad (2)$$

Here, γ indicates the isotropic and ξ the anisotropic bulk contribution to the SHG, and the i -directions are along the principal crystal axes.

For a crystalline surface of C_{3v} symmetry, excited by a single s-polarized pump beam at frequency ω , the total SH fields are then given by [7–9]:

$$E_{s,s}(2\omega) \sim (\chi_{\xi\xi\xi} - a\xi) \sin(3\psi), \quad (3a)$$

$$E_{p,s}(2\omega) \sim (\chi_{\perp\parallel\parallel} - \gamma) - b\xi \\ - c(\chi_{\xi\xi\xi} - a\xi) \cos(3\psi), \quad (3b)$$

where $E_{m,n}$ indicates the m -polarized SH response for a n -polarized pump beam. $\chi_{\xi\xi\xi}$ is the anisotropic and $\chi_{\perp\parallel\parallel}$ the isotropic surface contribution, \perp and \parallel indicate directions perpendicular and parallel to the surface respectively, ξ is parallel to $(11\bar{2})$ and a , b and c are complex numbers containing the Fresnel factors for reflection.

Eq. (3) shows how bulk and surface terms appear in exactly the same way, and therefore cannot be distinguished. Varying the angle of incidence will not solve this problem: it has been shown that both surface and bulk terms have the same angular dependence within a few percent [9,10]. One way to isolate the bulk anisotropic part is by measuring the SH response of a (100) surface, because due to inversion symmetry in the plane, the surface anisotropic term vanishes here. However, this method of comparing intensities is very sensitive for the quality of the different crystal surfaces. Also, it only gives the anisotropic terms.

3. Experiment

Our samples were optically flat Syton-etched and polished standard silicon wafers, cut with a small offset angle in the $(11\bar{2})$ direction and covered with a native oxide. It is well known that

such a vicinal Si surface exhibits a regular structure, with step-heights that are multiples of the double-layer spacing of 3.14 Å for Si(111) [11]. The interface sharpness and reproducibility of Syton-etched Si wafers has been seen in various SHG experiments: despite different sample sources, very similar SHG responses from such Si(111) samples have been observed [3,7,9,12]. This suggests that the etching process leaves only a narrow disordered Si layer that is totally consumed by the oxidation process, producing a sharp Si-SiO₂ interface showing the bulk Si symmetry, consistent with high resolution TEM [13,14] and photoemission experiments [15]. Consequently, for the oxidized vicinal surfaces, the Si-SiO₂ interface is also expected to exhibit a regular and sharp structure.

For the SHG experiment we used the frequency-doubled output at 532 nm of a seeded Q-switched Nd:YAG laser, incident at an angle of 45° on the sample. The fluence of the 8 ns pulses was limited to 50 mJ/cm², well below the damage threshold, and stable within 2%. The reflected SHG intensity was recorded while the samples were rotated about their normal at a constant rate. Three samples were studied, one precisely cut perpendicularly to the (111) direction, and two samples cut with offset angles of 3° and 5° respectively towards the $(11\bar{2})$ direction to get a regular step structure with two different step densities. The orientation of the samples was checked

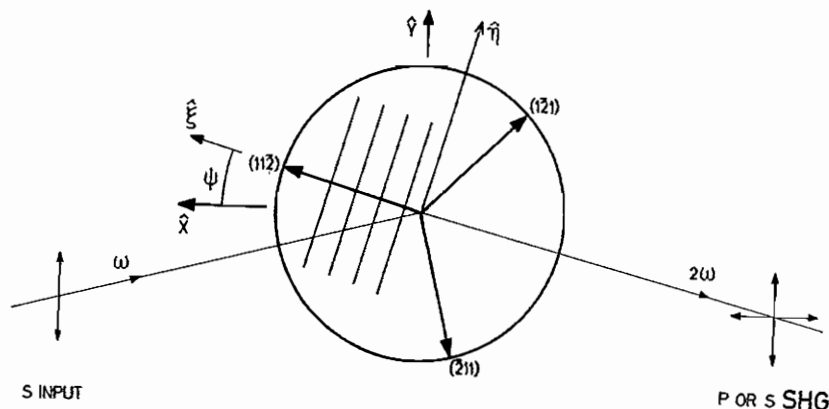


Fig. 1. Experimental geometry for the rotational anisotropy measurements. Indicated are the polarizations of the incoming and outgoing beams, the bond directions on the (111) surface and the direction of the steps. The rotation angle ψ is defined as the angle between the lab frame X -axis and the sample frame ξ -axis.

with X-ray diffraction. The rotation angle ψ was defined as the angle between the plane of incidence and $\hat{\xi}$ (see fig. 1).

4. Results and discussion

Fig. 2 shows the observed angular dependence of the s- and p-polarized SHG under s-polarized excitation. For $\theta = 0^\circ$ (i.e. for an unstepped surface), the observed signals are in perfect agreement with eqs. (3a) and (3b) and with those reported in the literature [3,7,9,12]. The data for the vicinal surfaces ($\theta = 3^\circ$ and $\theta = 5^\circ$) clearly deviate from this picture. Though still showing a resemblance to the original three-fold symmetry, the only real symmetry preserved is a mirror plane at 0° (along the $(11\bar{2})$ direction). This is exactly in accordance with the structure of these vicinal surfaces (see fig. 1). Cutting Si(111) with a small offset in the $(11\bar{2})$ direction leads to one broken

bond per atom at the step edges (at the Si-SiO₂ interface this bond is oxidized). Because of this broken bond the C_{3v} symmetry of a terrace is reduced to C_{1v} at the step edges, where the only preserved mirror plane is the one normal to the steps. For a C_{1v} symmetry, with $\hat{\xi} - \hat{z}$ being the mirror plane, $E_{s,s}(2\omega)$ in principle contains three independent nonvanishing tensor elements: $\chi_{\xi\xi\xi}$, $\chi_{\eta\xi\eta} = \chi_{\eta\eta\xi}$ and $\chi_{\xi\eta\eta}$, where $\hat{\eta}$ is perpendicular to $\hat{\xi}$ in the plane. Because of the net orientation of the broken bonds normal to the steps, the nonlinear response along the $\hat{\xi}$ -axis is expected to be dominating. Under this assumption, $\chi_{\xi\xi\xi}^{\text{step}}$ and $\chi_{\eta\xi\eta}^{\text{step}}$ will be small compared to $\chi_{\xi\xi\xi}^{\text{step}}$, and therefore will be neglected. Similarly, for $E_{p,s}$, the C_{1v} symmetry will lead to two extra nonvanishing terms: $\chi_{\xi\xi\xi}^{\text{step}}$ and $\chi_{\xi\xi\xi}^{\text{step}}$, which we assume to have the same phase. The total SHG response of the vicinal surface will then be a sum of the step contributions, showing C_{1v} symmetry and the terrace and bulk contributions showing C_{3v} symmetry. The

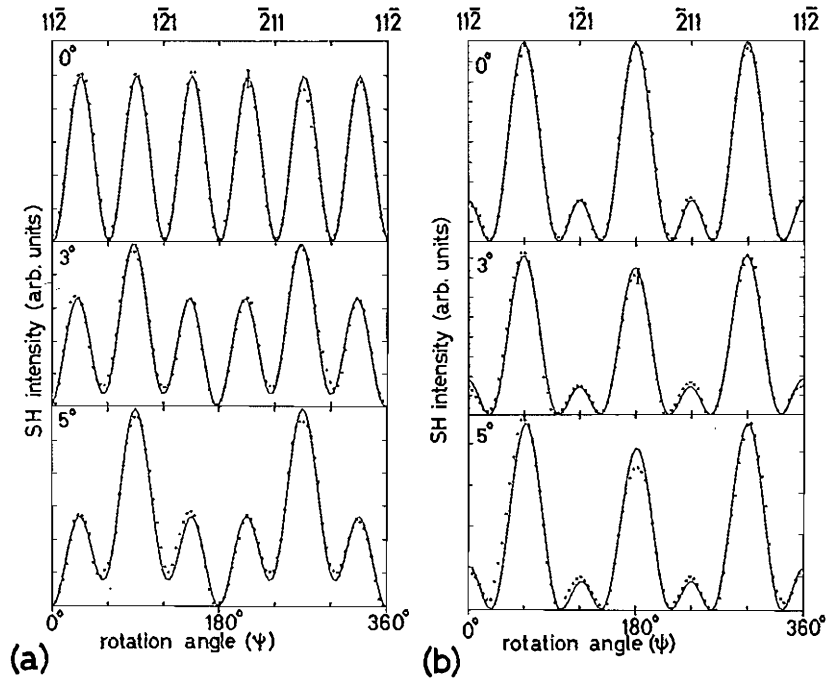


Fig. 2. SHG intensity from vicinal Si(111) surfaces as a function of the sample rotation angle ψ for two polarization combinations. (a) s-polarized SHG intensity for s-polarized pump. (b) p-polarized SHG intensity for s-polarized pump. The top traces (0°) show the C_{3v} symmetry, while the results for the two vicinal surfaces (offset angles 3° and 5°) show the interference of C_{3v} and C_{1v} symmetry. The dots are the experimental points, the solid lines a fit to eqs. (3) and (4).

SHG fields for a stepped Si(111) surface can then be written as:

$$E_{s,s} \sim [(1-x)\chi_{\xi\xi\xi} - a\xi] \sin(3\psi) + x\chi_{\xi\xi\xi}^{\text{step}} \sin^3(\psi), \quad (4a)$$

$$E_{p,s} \sim 1.41[(1-x)\chi_{\perp\parallel\parallel} - \gamma] - 0.18 e^{i66^\circ} [(1-x)\chi_{\xi\xi\xi} - a\xi] \cos(3\psi) + 0.70x\chi_{\xi\xi\xi}^{\text{step}} [1 - \cos(2\psi)] + 1.53 e^{i66^\circ} x\chi_{\xi\xi\xi}^{\text{step}} [\cos^3(\psi) - \cos(3\psi)], \quad (4b)$$

where x denotes the fraction of steps relative to the terraces, which depends on the offset angle θ , and the Fresnel factors for our specific geometry have been put in explicitly. For perfectly sharp step edges x can be estimated to be the ratio of an atomic dimension to the size of the terrace. For $\theta = 3^\circ$ and 5° we determined x to be 0.026 and 0.048 respectively. Using eq. (4a) the experimental data can now be fitted by $E_{s,s} = A \sin(3\psi) + B e^{i\Phi} \sin^3(\psi)$, where Φ denotes the phase difference between the step and terrace contributions. By Fourier analysis of the data it was further checked that no other symmetry components were present.

Because we can now determine A/B for the two different values of the step concentration x , we can find values for $\chi_{\xi\xi\xi}^{\text{step}}$ and $a\xi$ relative to the surface component $\chi_{\xi\xi\xi}$. The results are: $\chi_{\xi\xi\xi}^{\text{step}} = -7.0 e^{i100^\circ} \chi_{\xi\xi\xi}$ and $a\xi = 1.3\chi_{\xi\xi\xi}$ [16]. This calculation does not depend critically on the choice of x . If x is doubled, $\chi_{\xi\xi\xi}^{\text{step}}$ stays the same and $a\xi$ changes to $1.6\chi_{\xi\xi\xi}$. The surface and bulk anisotropic terms are found to be of the same order of magnitude, which is in reasonable agreement with the results of Tom, who found $a\xi = 0.3e^{-i22^\circ}$ by comparing SHG signals from Si(111) and Si(100) surfaces [7]. The data of $E_{p,s}$ for the stepped surfaces can be fitted with

$$E_{p,s} = A - \cos(3\psi) + e^{i\Phi_1} \{ B [1 - \cos(2\psi)] + C e^{i\Phi_2} [\cos^3(\psi) - \cos(3\psi)] \}.$$

From the ratio B/A for the two different step densities we find $\chi_{\xi\xi\xi}^{\text{step}} = -7.0 e^{i100^\circ} \chi_{\xi\xi\xi}$. Using

the value of $a\xi$ which was determined from $E_{s,s}$ we can obtain values for the isotropic surface and bulk contributions separately. We find $\chi_{\perp\parallel\parallel} = 1.3 e^{i66^\circ} \chi_{\xi\xi\xi}$ and $\gamma = -2.0 e^{-i18^\circ} \chi_{\xi\xi\xi}$. This means that also for the isotropic part, the surface and bulk contributions are found to be of the same order of magnitude. Tom found $\chi_{\perp\parallel\parallel} - \gamma = -1.9 e^{i108^\circ} \chi_{\xi\xi\xi}$ but could not separate them [7]. We find $\chi_{\perp\parallel\parallel} - \gamma = -2.4 e^{i193^\circ} \chi_{\xi\xi\xi}$.

The observed step terms are found to be an order of magnitude larger than the anisotropic surface term. This should be related to the very anisotropic environment of the bonds at the step edges. A more detailed study of this interesting observation is presently in progress.

In conclusion, the steps on vicinal Si(111) surfaces have a very strong effect on the rotational anisotropy of the SHG from these surfaces. In this way the surface and bulk contributions to the SHG could be determined separately. In the present analysis however we have neglected the fact that the reflected light obeys Snell's law with respect to the macroscopic surface, which has an offset from the (111) plane. The resulting "wobbling" will have a similar effect on the rotational dependence as the steps. Taking this effect into account the values of $\chi_{\xi\xi\xi}^{\text{step}}$ and $a\xi$ decrease, but stay of the same order of magnitude. The conclusions presented above remain the same. Both the anisotropic and isotropic surface and bulk contributions are found to be of the same order of magnitude for the Si-SiO₂ interface. These measurements show that SHG is a very sensitive probe for the microscopic structure and symmetry properties of surfaces.

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